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(54) Abstract Title: **Microcapsules with siloxane walls formed in situ**

(57) A lipophilic cosmetic, chemical, biological or pharmaceutical active material composition is encapsulted by mixing it with a water reactive silicon compound and emulsifying the mixture in an aqueous medium under shear and in the presence of at least one surfactant, thereby forming an aqueous suspension of microcapsules having a core of the active material composition surrounded by a shell of silicon-based network polymer.

The polysiloxane shell is preferably made by condensation of a tetraalkoxy- or trialkoxy-alkylsilane such as tetraethoxysilane (TEOS).

The preferred active material is a sunscreen.

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ENCAPSULATION PROCESS AND ENCAPSULATED COMPOSITIONS

FIELD OF THE INVENTION

[0001] This invention relates to a process for encapsulating materials such as cosmetic, chemical, biological or pharmaceutical active material compositions and to the encapsulated compositions which can be formed thereby. It is of particular use in encapsulating sunscreen active materials and can also be used for other cosmetic actives, such as perfumes, for other chemical materials and for pharmaceutical active materials.

[0002] In some personal care products, the cosmetic active material may be present in high amounts. For example, a SPF (sun protection factor) 15 sun cream or lotion may contain over 5% by weight sunscreen active materials (UV blockers). Moreover, some cosmetic active materials, including UV blockers, can be skin irritants or should not be absorbed through the skin. There is a need for products which prevent or inhibit skin contact by such a cosmetic active material.

BACKGROUND TO THE INVENTION

[0003] US-A-6303149 describes a process for preparing sol-gel microcapsules loaded with functional molecules by emulsifying sol-gel precursors and the functional molecules in an aqueous solution, and mixing the emulsion with an acidic, neutral or basic aqueous solution to obtain a suspension of microcapsules. US-A-6238650 describes a sunscreen composition comprising at least one sunscreen active ingredient and a cosmetically acceptable vehicle, wherein said sunscreen active ingredient is in the form of sol-gel microcapsules containing at least one sunscreen compound. The sol-gel microcapsules are prepared by the method disclosed in US-A-6303149.

[0004] EP-A-941761 describes a process for preparing microcapsules with an organopolysiloxane shell and a core material, in which the shell is formed in situ by hydrolysis and polycondensation of an organosilane and/or a condensation product thereof having at most 4 silicon atoms.

[0005] WO-A-03/066209 describes a process for encapsulating a lipophilic cosmetic, chemical, biological or pharmaceutical active material composition, characterised in that a water reactive silicon compound comprising tetraalkoxysilane is added to an aqueous emulsion of the active material composition having a positive zeta-potential, whereby the tetraalkoxysilane condenses and polymerises at the interface of the emulsified droplets of the lipophilic active material composition to form microcapsules having a core of the active material composition surrounded by a shell of silicon-based network polymer.

[0006] There is a need for cosmetic active materials, particularly sunscreens, in a form in which the active material is inhibited from skin contact but which contains a high proportion of the active material and can readily be incorporated into a cosmetic preparation such as a lotion or cream.

SUMMARY OF THE INVENTION

[0007] According to the present invention, a process for encapsulating a lipophilic cosmetic, chemical, biological or pharmaceutical active material composition, characterised in that the active material composition is mixed with a water reactive silicon compound and the mixture is emulsified in an aqueous medium under shear and in the presence of at least one surfactant, thereby forming an aqueous suspension of microcapsules having a core of the active material composition surrounded by a shell of silicon-based network polymer. We use the term 'emulsion ' to mean a liquid in liquid dispersion and 'suspension' to mean a solid in liquid dispersion.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The water reactive silicon compound preferably comprises a tetraalkoxysilane or alkyl trialkoxy silane or a liquid condensate thereof, most preferably a tetraalkoxysilane such as tetraethoxysilane (also known as tetraethyl orthosilicate or TEOS). The tetraalkoxysilane such as TEOS can be used in monomeric form or as a liquid partial condensate. The tetraalkoxysilane can be used in conjunction with one or more other water-reactive silicon compound having at least two, preferably at least 3, Si-OH groups or

hydrolysable groups bonded to silicon, for example an alkyltrialkoxysilane such as methyltrimethoxysilane or a liquid condensate of an alkyltrialkoxysilane. Hydrolysable groups can for example be alkoxy or acyloxy groups bonded to silicon. The water reactive silicon compound can for example comprise 75-100% by weight tetraalkoxysilane and 0-25% trialkoxysilane. The alkyl and alkoxy groups in the tetraalkoxysilanes or other silanes preferably contain 1 to 4 carbon atoms, most preferably 1 or 2 carbon atoms. The tetraalkoxysilane, and other water-reactive silicon compound if used, hydrolyses and condenses to form a network polymer, that is a 3-dimensional network of silicon-based material, around the emulsified droplets of the lipophilic active material composition. The water-reactive silicon compound preferably consists of at least 75%, and most preferably 90-100% tetraalkoxysilane. We have found that a tetraalkoxysilane is the most effective silicon compound for forming impermeable microcapsules, forming a 3-dimensional network consisting substantially of $SiO_{4/2}$ units.

[0009] The lipophilic cosmetic, chemical, biological or pharmaceutical active material composition is a liquid at the time it is emulsified and usually is liquid at ambient temperature. It can be an undiluted liquid active material or can be a solution of an active material in a lipophilic solvent, preferably a non-volatile solvent, or a water-in-oil or oil-in-water-in-oil emulsion, or a lipophilic suspension. Solid active materials can be melted before being emulsified if their melting temperature is significantly below 100°C.

[0010] The active material can for example be a sunscreen. Sunscreen active compounds which are used in the invention can for example be UV-B blockers such as 2-ethylhexyl methoxycinnamate, generally known as octyl methoxycinnamate or UV-A blockers such as butylmethoxydibenzoylmethane known as avobenzone. Mixtures of sunscreen compounds can be used, for example a mixture of octyl methoxycinnamate with octocrylene, although octyl methoxycinnamate and avobenzone are known to be photolytically unstable when mixed in high concentrations and should preferably not be encapsulated together. Octyl methoxycinnamate is liquid and can be used undiluted. Butylmethoxydibenzoylmethane is a solid which can be dissolved in an inert lipophilic liquid.

[0011] Sunscreen active compounds can perform their function of screening out harmful UV radiation while they are encapsulated. The silicon-based polymer forming the shell of the microcapsules does not absorb UV and has no negative impact on the sunscreen efficiency, and may potentially improve the protection against photodegradation. An encapsulated sunscreen according to the invention preferably has a substantially impermeable silicon-based polymer shell.

[0012] Another type of cosmetic active material which can be encapsulated is a perfume. In this case the active material composition which is mixed with the water reactive silicon compound may comprise a diluent as well as the active perfume or fragrance compounds. The diluent is preferably odourless and non-volatile and can for example be a non-reactive polydiorganosiloxane or a nonvolatile liquid hydrocarbon or ester. When encapsulating perfume, a permanent shell is not required. The shell may be breakable, for example brittle, so that the microcapsules are broken under the application of shear, releasing the perfume. Larger particles of diameter at least 10μm, for example 50μm or above, are more readily breakable than smaller particles.

[0013] Other examples of active materials which may be encapsulated are UV absorbers for use in coatings, paints, plastics materials, sealants or textile finishes to improve weatherability and resist fading (such UV absorber compositions are preferably encapsulated in an impermeable silicon-based polymer shell), pharmaceuticals or sensitive chemical materials. Pharmaceuticals and related health products such as vitamins can be encapsulated in a silicon-based polymer shell which is broken down in the body after ingestion of the pharmaceutical. Biological (including biochemical) materials such as proteins, enzymes and cells can similarly be encapsulated. Radioactive material can be encapsulated for cancer treatment. Water insoluble liquid chemical materials can be protected, for example during storage or transport. Encapsulation can alternatively be used to modify the surface properties, optical properties or feel and taste of any core material.

[0014] The active material composition and the water reactive silicon compound should be thoroughly mixed as an oil phase in the absence of water; this can easily be achieved by stirring if both components are liquid. The weight ratio of active material

composition to water reactive silicon compound is generally at least 1:1 and preferably at least 2:1, most preferably in the range 2.5:1 to 5:1 or even as high as 25:1. For a sunscreen, the weight ratio of sunscreen active compound(s) to water reactive silicon compound and hence to the silicon based polymer shell of the microcapsules is preferably at least 1.5:1.

[0015] The resulting oil phase is emulsified in an aqueous medium with the aid of a surfactant. The mixture is agitated as the oil phase is added to the water so that the oil phase is dispersed as droplets. Mixing can for example be by stirring, but it is preferred that the oil phase and aqueous surfactant solution are mixed with high shear, for example in a mixer of the rotor and stator type such as a Silberson (trade mark) mixer The water reactive silicon compound reacts to form a silicon-based polymer at the water interface, gradually forming a shell of silicon-based network polymer which surrounds the active material composition, e.g. the sunscreen. The product thus comprises an aqueous suspension of microcapsules having a core of the active material composition surrounded by a shell of silicon-based polymer.

[0016] The surfactant is most preferably a cationic or amphoteric surfactant, which readily forms an emulsion of positive zeta-potential. We have found that a positive zeta-potential promotes condensation and polymerisation of the tetraalkoxysilane at the interface of the emulsified droplets of the lipophilic active material composition, leading to more impervious microcapsules. Nonionic surfactants can be used; for example the cationic or amphoteric surfactant can be mixed with up to an equal weight of nonionic surfactant.

[0017] The concentration of surfactant in the aqueous emulsion can be between 0.01 and 10% by weight, but is preferably at least 0.02% and below 2%, most preferably 0.05 to 1.5% by weight of the emulsion, particularly 0.2-1.0%. We have found in general that the use of low levels of surfactant during emulsification of the lipophilic active material and reaction with the alkoxysilane leads to microcapsules which are more resistant to diffusion or leaching of the lipophilic active material from the microcapsules. Subsequent addition of surfactant to the suspension of microcapsules has less or no effect on diffusion or leaching of the lipophilic active material from the microcapsules.

[0018] The weight ratio of oil phase to aqueous phase in the emulsion can generally be between 40:1 and 1:50, although the higher proportions of aqueous phase are economically disadvantageous particularly when forming an emulsion of microcapsules. Usually the weight ratio of oil phase to aqueous phase is between 2:1 and 1:3. If the active material composition is highly viscous, a phase inversion process can be used in which the oil phase is mixed with surfactant and a small amount of water, for example 2.5 to 10% by weight based on the oil phase, forming a water-in-oil emulsion which inverts to an oil-in-water emulsion as it is sheared. Further water can then be added to dilute the emulsion to the required concentration.

[0019] Examples of cationic surfactants include quaternary ammonium hydroxides such as octyl trimethyl ammonium hydroxide, dodecyl trimethyl ammonium hydroxide, hexadecyl trimethyl ammonium hydroxide, octyl dimethyl benzyl ammonium hydroxide, decyl dimethyl benzyl ammonium hydroxide, didodecyl dimethyl ammonium hydroxide, dioctadecyl dimethyl ammonium hydroxide, tallow trimethyl ammonium hydroxide and coco trimethyl ammonium hydroxide as well as corresponding salts of these materials, fatty amines and fatty acid amides and their derivatives, basic pyridinium compounds, quaternary ammonium bases of benzimidazolines and polypropanolpolyethanol amines. Cationic emulsions of microcapsules have increased deposition of the microcapsules from the emulsion and increased substantivity on both hair and skin.

[0020] Examples of suitable amphoteric surfactants include cocamidopropyl betaine, cocamidopropyl hydroxysulfate, cocobetaine, sodium cocoamidoacetate, cocodimethyl betaine, N-coco-3-aminobutyric acid and imidazolinium carboxyl compounds.

[0021] The above surfactants may be used individually or in combination.

[0022] Examples of non-ionic surfactants include polyoxyalkylene alkyl ethers such as polyethylene glycol long chain (12-14C) alkyl ether, polyoxyalkylene sorbitan ethers, polyoxyalkylene alkoxylate esters, polyoxyalkylene alkylphenol ethers, ethylene glycol propylene glycol copolymers, polyvinyl alcohol and alkylpolysaccharides, for example materials of the structure R^1-O-$(R^2O)_m$-$(G)_n$ wherein R^1 represents a linear or branched alkyl

group, a linear or branched alkenyl group or an alkylphenyl group, R^2 represent an alkylene group, G represents a reduced sugar, m denotes 0 or a positive integer and n represent a positive integer as described in US Patent 5,035,832.

[0023] The continuous phase of the emulsion can be a mixture of water with a water-miscible organic solvent such as an alcohol or lactam provided that the continuous phase is not miscible with the lipophilic active material. The particle size of the emulsion of lipophilic active material can be reduced before addition of the water-reactive silicon compound, for example in an apparatus applying increased shear such as a homogeniser or microfluidiser, or a sonolator (ultrasonic mixer), producing an emulsion of microcapsules of particle size 100-1000 nm, most preferably between 200 nm and 500 nm. The emulsion can alternatively be prepared by phase inversion.

[0024] The particle size of the suspension of microcapsules is dependant on the degree of shear applied during addition of the oil phase and on the level of surfactant, and is generally in the range 0.01 to 500, preferably 0,1 to 50 micrometres, most preferably 200 nm to 10 µm. The particle size of the emulsion formed initially by mixing the oil and aqueous phases can be reduced in a subsequent processing step, which can for example be carried out in an apparatus applying increased shear, or in a homogeniser in which an emulsion is pumped at high velocity through a narrow nozzle into a high pressure chamber where it impinges on a surface, or in a sonolator (ultrasonic mixer). The homogeniser may be of the microfluidiser type in which two high velocity streams of the emulsion impinge on each other in the high pressure chamber before impinging on a fixed surface. This processing step reduces the particle size of the emulsion, producing an emulsion of microcapsules of particle size 100-1000nm, most preferably between 200nm and 500nm, with increasing pressure leading to a smaller particle size.

[0025] For some uses, microcapsules of particle size 1-500 µm, particularly up to 50 or 100 µm, may be preferred. If a suspension of this particle size is required, the aqueous phase to which the oil phase is added preferably contains a thickener, for example polyvinylpyrrolidone, polyvinyl alcohol, bentonite clay, a cellulose derivative, particularly a cellulose ether such as sodium carboxymethylcellulose, a lightly crosslinked acrylic polymer,

modified starch, an alginate or xanthan gum, to inhibit settling of the microcapsules from the emulsion during formation or subsequently.

[0026] The condensation reaction forming the microcapsules is generally carried out at ambient temperature and pressure, but can be carried out at increased temperature, for example up to 95°C, and increased or decreased pressure, for example under vacuum to strip the volatile alcohol produced during the condensation reaction.

[0027] A catalyst for hydrolysis and/or condensation of the water reactive silicon compound to form the silicon-based polymer may be used. The catalyst is preferably an oil soluble organic metal compound, for example an organic tin compound, particularly an organotin compound such as a diorganotin diester, for example dimethyl tin di(neodecanoate), dibutyl tin dilaurate or dibutyl tin diacetate, or alternatively a tin carboxylate such as stannous octoate, or an organic titanium compound such as tetrabutyl titanate. An organotin catalyst can for example be used at 0.05 to 2% by weight based on the water reactive silicon compound. An organotin catalyst has the advantage of effective catalysis at neutral pH. A catalyst is most preferably mixed with the lipophilic cosmetic, chemical or pharmaceutical active material composition before it is emulsified, since this promotes condensation of the water reactive silicon compound at the surface of the emulsified lipophilic droplets. Encapsulation can however be achieved without catalyst, and we have found in some cases that microcapsules formed with a low level of catalyst or no catalyst are more resistant to diffusion or leaching of the lipophilic active material from the microcapsules.

[0028] The aqueous continuous phase of the aqueous suspension of microcapsules can contain water miscible organic solvent; for example it usually contains an alcohol such as ethanol generated by hydrolysis of Si-bonded alkoxy groups. It may be advantageous to incorporate the suspension of microcapsules in a water based treatment composition, for example a cosmetic, chemical or pharmaceutical composition, direct into the water-based treatment composition without separating the microcapsules from the suspension. In particular, a suspension of encapsulated sunscreen can be incorporated direct into a sunscreen lotion or cream or can even be used itself as a sunscreen lotion. The suspension of

encapsulated sunscreen can be used in conjunction with other sunscreens, if desired. For example, an encapsulated UV-B absorber such as octyl methoxycinnamate can be formulated with a UV-A absorber such as avobenzone and optionally with other sunscreens. The UV-A absorber in such a formulation can be free or encapsulated.

[0029] For many uses it may be preferred to recover the microcapsules from suspension, for example for subsequent dispersion in a different medium. We have found that the microcapsules can readily be separated from the suspension, for example by filtration, without addition of acid or base to the emulsion. Recovery of the microcapsules can be achieved by any known liquid removal technique, for example by spray drying, spray chilling, filtering, oven drying or lyophilisation.

[0030] Separated microcapsules of an encapsulated sunscreen can for example be dispersed in a water based cosmetic preparation, preferably in such a proportion that the content of sunscreen in the cosmetic preparation is 0.1 to 10% by weight. Alternatively the microcapsules can be redispersed in an organic solvent, optionally with additives such as surfactant and/or polymer.

[0031] Alternative uses of encapsulated sunscreens according to the invention are in fabric treatment, for example the suspension of microcapsules or the separated microcapsules can be incorporated in a fabric softener to inhibit subsequent colour fading of the fabric, or in plastics compositions or coatings which are designed to be exposed to sunlight or UV light in use.

[0032] The encapsulated product can be post-treated with a water-reactive metal alkoxy or acyloxy compound. The metal compound should be gradually hydrolysed in water rather than immediately reacting with water; compounds of Group IVB, IVA or VA of the Periodic Table are suitable such as compounds of silicon, titanium, zirconium or vanadium. The water-reactive metal alkoxy or acyloxy compound can for example harden the shell of the microcapsules and/or make them more impermeable. The reactive metal alkoxy or acyloxy compound can for example be an alkoxysilane or acyloxysilane, particularly a trialkoxysilane such as methyl triethoxy silane or isobutyl triethoxy silane, or a silane having Si-H

functionality such as tris(dimethylhydrogensilyloxy) n-octyl silane, or alternatively a titanium alkoxide (alkyl titanate).

[0033] The reactive metal alkoxy or acyloxy compound can have an organic functional group to promote adhesion to substrates, especially textile substrates, for example 3-methacryloxypropyl trimethoxy silane, 3-aminopropyl triethoxysilane, 3-aminopropyl trimethoxy silane, 3-glycidoxypropyl trimethoxy silane and 3-(2-aminoethylamino)propyl trimethoxy silane. The microcapsules can be post-treated with a reactive metal alkoxy or acyloxy compounds, e.g. an alkoxysilane to change their physical and/or chemical properties, for example by making the capsule surface more hydrophobic or more hydrophilic. For example, the microcapsule surface can be made more hydrophobic by reaction with a silane having a long chain alkyl group such as octyl triethoxy silane. As an alternative to chemical reaction the microcapsules can be coated with a material which alters their surface properties. The surface treatment can be carried out on the microcapsules in suspension or on the separated solid microcapsules.

[0034] The microcapsules according to the invention inhibit diffusion or leaching of the lipophilic cosmetic, chemical, biological or pharmaceutical active material from the microcapsules. When encapsulating sunscreen, for example, it is preferred that the rate of diffusion or leaching is as low as possible. For other lipophilic active materials a controlled rate of release may be preferred, and this can be achieved by adjusting the level of surfactant, the level of tetraalkoxysilane and optionally of trialkoxysilane, the particle size and the level of catalyst.

[0035] Microcapsules according to the invention containing cosmetic active material compositions, including sunscreens, have good skin adhesion. The microcapsules minimise contact between the sunscreen and the skin, resulting in decreased penetration and consequently less potential irritation and allergy. The emulsion of microcapsules can have a high concentration of sunscreen (high pay load) compared to an aqueous dispersion of sunscreen, increasing the ease of use of lipophilic sunscreens in surfactant based product and allowing the sunscreen preparation to have a very liquid product form, which may be sprayable. Encapsulation eliminates the greasy feel associated with lipophilic sunscreens.

increasing the acceptability and use in skin care products. The microcapsule does not affect the photostability of the encapsulated sunscreen. The silicon-based polymer forming the shell of the microcapsules generally remains water insoluble even in the presence of surfactant, so that the encapsulated cosmetic active can be used in water based toiletry preparations including surfactant based products such as hair shampoo, conditioner or colourant, textile softener, detergent or shower gel.

[0036] The invention is illustrated by the following Example in which parts and percentages are by weight:

Example

[0037] 0.31 parts Volpo L3 (Trade Mark) nonionic polyethylene glycol lauryl ether surfactant and 0.14 parts Arquad 16-29 (Trade Mark) cetyl trimethyl ammonium chloride cationic surfactant were mixed with 54.09 parts water and stirred for 20 minutes at 400rpm to dissolve the surfactants. 35.00 parts octylmethoxycinnamate (OMC, a UV-B sunscreen oil) was mixed with 10.46 parts TEOS and the resulting oil phase was added to the surfactant solution while stirring at 500rpm for 15 minutes. The resulting emulsion was passed once through a Rannie homogeniser at 900 bars, and then stirred at 400rpm overnight. A suspension of microcapsules was produced.

CLAIMS

1. A process for encapsulating a lipophilic cosmetic, chemical, biological or pharmaceutical active material composition, characterised in that the active material composition is mixed with a water reactive silicon compound and the mixture is emulsified in an aqueous medium under shear and in the presence of at least one surfactant, thereby forming an aqueous emulsion of microcapsules having a core of the active material composition surrounded by a shell of silicon-based network polymer.

2. A process according to Claim 1, characterised in that the water reactive silicon compound comprises a tetraalkoxy silane or alkyl trialkoxy silane or a liquid condensate thereof.

3. A process according to Claim 2, characterised in that the water reactive silicon compound comprises tetraethyl orthosilicate.

4. A process according to any of Claims 1 to 3, characterised in that the active material composition is mixed with a water reactive silicon compound at a weight ratio of at least 1.5:1.

5. A process according to any of Claims 1 to 4, characterised in that the surfactant comprises at least one cationic or amphoteric surfactant

6. A process according to any of Claims 1 to 5, characterised in that the concentration of surfactant in the emulsion is 0.02 to 2.0% by weight of the emulsion.

7. A process according to any of Claims 1 to 6, characterised in that the microcapsules are separated from the emulsion without addition of acid or base to the emulsion.

8. A method of producing a water-based treatment composition characterised in that an aqueous emulsion of microcapsules having a core of lipophilic active material surrounded by a shell of silicon-based polymer is prepared according to any of Claims 1 to 6 and is incorporated direct into the water-based treatment composition without separation of the microcapsules from the emulsion.

9. A method according to Claim 8 for preparing a sunscreen lotion, characterized in that the lipophilic active material is a sunscreen.